Journal of Power Sources 222 (2013) 188–195

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Research of hydrogen generation by the reaction of Al-based materials with water

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HIGHLIGHTS

► The inert alumina film is prevented from forming on the Al surface by adding CaO.
► The Al-based materials can rapidly react with water to produce hydrogen.
► The Al-based materials are very cheap and are easily prepared by ball milling.

ARTICLE INFO

Article history:
Received 27 June 2012
Received in revised form
24 August 2012
Accepted 27 August 2012
Available online 3 September 2012

Keywords:
Hydrogen generation
Al-based materials
Ball milling
Hydrogen yield

ABSTRACT

Al, CaO and salt powder mixtures are used as the starting materials to prepare the Al-based materials by the mechanical ball-milling method for hydrogen generation. The effects of preparation and reaction parameters on the hydrogen generation are investigated in this paper. With increasing ball milling time, the Al crystallite size is reduced and the reaction activity of Al is improved. But the overlong ball milling time easily causes the oxidation of Al and decreases its hydrogen yield. CaO can provide OH^- for the hydrogen generation reaction by hydrolysis. Increasing the NaCl addition can accelerate the activation of Al and promote its hydrogen generation. In the water containing chloride ions and sulfate ions, the hydrogen generation rate is obviously improved. But Mg^{2+} ions will reduce the hydrogen yield due to its strong affinity to OH^-. The maximum hydrogen yield is gained in the water at 30 °C There are some CaO on the surface of Al particle in the Al-based materials, which can improve the air oxidation resistance in air. Storing the Al-based materials in air with relative humidity of 50% at 30 °C for 40 h, the hydrogen yield is still kept at 89%.

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1. Introduction

Hydrogen, a regenerative fuel with high calorific value, has attracted much attention by scientists [1,2]. It can become one of the most promising alternatives to fossil fuels in future [3,4]. Hydrogen can be consumed in a fuel cell, converting chemical into electrical energy with high efficiencies in the mild conditions, and can also be cleanly burned in the internal combustion engines [5]. However, hydrogen is a secondary source of energy and does not exist in nature. It must be produced from some compounds containing H [6]. These compounds mainly include fossil fuel, NH_3, CH_4, metal hydrides, water and other hydride. Water is the most abundant resource on the earth and can supply a great amount of raw materials for producing hydrogen. Many methods are used to split water to produce hydrogen, such as water electrolysis [7], water photocatalysis [8], metal hydrides hydrolysis and metal hydrolysis [9–12]. However, hydrogen must first be produced in the hydrogen plants by water electrolysis or water photocatalysis and then is stored and delivered to users by the pipe or tank. There are some potential hazards in the process of storage and delivery because hydrogen is a kind of flammable and explosive gas. Therefore, developing a new method for the rapid production and safe storage of hydrogen is very crucial.

Some metal or metal hydrides can directly react with water to produce hydrogen through the hydrolysis reaction. These materials are easily stored and delivered to users. So the "on-board" production of hydrogen can be realized. Although these metal hydrides such as $NaBH_4$ and KBH_4 can be directly used to produce hydrogen by reacting with water, noble metals must be used in the reaction as catalysts. Additionally, the preparation process of $NaBH_4$ or KBH_4 is very complex [13–15]. So these materials cannot be applied in the practical hydrogen production. Now, metal and its alloy have been

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http://dx.doi.org/10.1016/j.jpowsour.2012.08.078

used to produce hydrogen through hydrolysis reaction by many researchers. Compared with other metals, aluminum has good activity and has very cheap price due to abundant in earth. It's very important that Al metal has low atomic weight (27 g mol^{-}) and 3 valence electrons [16]. Therefore, the hydrogen density (hydrogen production of unit mass materials) of Al is very high and reaches 11.1%. The energy capacity of Al reaches 2980 Ah kg^{-1}. 27 g or 1 mol of Al can produce 1.5 mol of hydrogen. Actually, Al can be regarded as convenient portable energy-storage metal. By the Hall–Heroult process, some energy, such as hydroelectric power, wind power and solar, can be converted to store in the Al metal. The Al metal can be safely delivered to the region with lack of energy. Especially, when the primary energy is very abundant and cannot be utilized completely, the redundant energy can be converted to store in the form of Al metal. The stored energy is released in form of hydrogen by the reaction of Al and water. Therefore, Al can be the most promising materials for producing hydrogen.

However, aluminum cannot directly react with water to produce hydrogen, although aluminum has very high reaction activity. The inert oxide film formed on the surface can prevent the hydrolysis reaction [17]. In order to improve the reaction rate of Al with water, many methods are used to destroy the dense oxide layer by researchers [18,19]. For example, some researchers adopt the alkaline or sodium aluminate solution to dissolve the inert oxide film. Under this condition, Al can react quickly to produce hydrogen. However, these reagents are highly corrosive and can corrode the reaction equipment. Al–Ga alloy prepared by Woodall can destroy alumina layer effectively [20]. But Ga does not produce hydrogen by itself, which will decrease the energy efficiency of alloy. In addition, the content of Ga in earth is very low, and its price is very high. So the method cannot be applied massively to produce hydrogen. Other researchers prepare the aluminum–ceramic composites powder by ball milling the mixture of Al and Al_2O_3 or $Al(OH)_3$. But in order to improve the reaction activity of Al, 90% Al_2O_3 is added. On this condition, the hydrogen production of unit mass is reduced greatly [6]. In addition, some high-priced rare metals are used to prepare the Al-based alloy [21–23]. Although it can improve the hydrogen generation of Al, the cost is too high, and its byproduct with complex composition is hard to be recycled.

In our former research, we find the calcium, a kind low-priced metal, can effectively eliminate the inert oxide film on the surface of Al metal [24]. Through analyzing the mechanism of action of Ca in the reaction process of Al–Ca alloy, it inspired us to find a more low-cost substance, calcium oxide, to activate Al. Calcium oxide can react with water to release heat and to produce OH^{-}, which will be beneficial to promote the hydrogen generation of Al in the water. The mechanism of action resembles that of Ca during the hydrolysis reaction. In this research, we will prepare a new Al-based material, Al–CaO–salt, by the ball milling method. The effect of preparation and reaction parameters on the hydrogen generation will be investigated in this paper.

2. Experimental

Al (99.9 wt%, analytical grade, 74 μm), CaO (99.9 wt%, analytical grade, 60 μm) and NaCl (99.8 wt%, analytical grade, 140 μm) are used as the starting materials. The Al-based materials are prepared by the ball milling method. Ball milling is performed in the planetary ball miller (Qm-1SP-2, Nanjing University Instrument Plant, China), equipped with stainless steel milling jars 500 ml and steel balls 4–5 mm in diameter. In each experiment, firstly 30 g Al, CaO and NaCl mixture with different composition is charged into jars, and then 300 g steel balls (ball to mixture mass ratio is fixed 10:1) are added. During the process of ball milling, the rotational milling speed is kept 512 rpm and the milling time varies from 30 min to 120 min. The phase composition of Al-based material is determined by the X-ray diffraction pattern (XRD, Dmax/2550VB+, Rigaku Corporation, Japan). Scanning electron microscope (SEM, JSM-5600, JEOL, Japan) is used to observe the surface morphology of samples.

The hydrogen generation reactions of Al-based materials are carried out in a plastic reactor of 50 ml. In each experiment, 0.5 g of Al-based powder is first placed in the reactor. And then 20 ml of water is charged into the reactor. The generated H_2 flows through a water bath at room temperature in order to cool H_2 gas and then flows through a pipe filled with CaO in order to dry H_2 gas. The volume of H_2 gas is measured by the water displacement method. H_2 gas is collected in a container filled with water, and water is displaced into a 500 ml of flask through a pipe connected with this container. The mass of flask with water displaced by H_2 gas is measured by electronic balance (UX2200H, Shimadzu Corporation, Japan). The drawing of experimental apparatus is presented in Fig. 1. The electronic balance connects with a computer, which can record these quality data automatically. The data is just the quantity of water displaced by H_2 gas, namely the volume of generated H_2. Under the condition of 1 atm and 25 °C, the volume of one mol H_2 is 24.45 L. In the Al-based materials, only Al can produce hydrogen. As the content of Al is a% in materials, the hydrogen yield is calculated as follows:

$$\text{Hydrogen yield}/\% = \frac{\text{volume of generated } H_2}{(a\%/27) \times 1.5 \times 24.45 \times 0.5} \times 100\% \quad (1)$$

In the process of hydrogen generation, different salt solution and different initial temperature water is used to produce hydrogen in order to investigate the effects.

3. Results and discussion

3.1. Effect of ball-milling on the hydrogen generation

High-energy mechanical ball-milling is a solid-state powder processing technique involving repeated welding and fracturing of

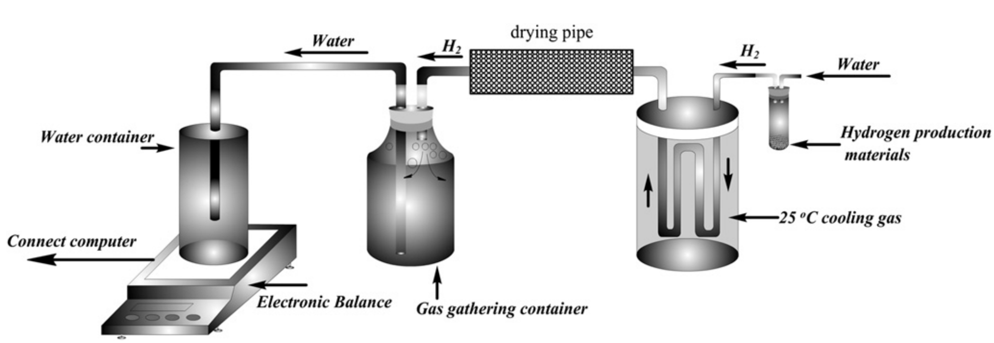

Fig. 1. The drawing of experimental apparatus.

powder particles. It can change the particles' microstructure and cause many various defects, such as dislocations, vacancies and grain boundaries, which create many fresh surfaces on the Al particles [5,25]. These fresh surfaces with defects possess very high reaction activity. In addition, the alloy particle size will decrease during the process of high-energy ball milling by the repeated grain break, cold welding and re-welding [22]. After the ball milling, the hydrogen generation of Al reacting with water can be improved. To investigate the effect of ball-milling on the hydrogen generation, Al, CaO and salt powder mixtures are ball-milled from 0.5 h to 2.0 h to prepare the Al-based materials, and then the Al-based materials contact with water to produce hydrogen. Fig. 2 is the hydrogen generation curves of Al-based materials ball-milled for different times. From Fig. 2, the total reaction process mainly includes three steps, induction reaction period, rapid reaction period and low reaction period. Although the composition is different, the effect of ball milling time on the hydrogen generation almost is same. As the ball milling time increases from 0.5 h to 1.0 h, their induction period begins to increase slowly. Prolonging the ball milling time to 2.0 h, the induction periods increase to 1500 s for sample (a) and 1750 s for sample (b), respectively. The increase of induction period is probably because more Al particles are coated by the CaO with increasing ball milling time. The CaO layer decreases the access of water to the surface of Al. So the induction period is prolonged with increasing ball milling time. Additionally, the results show that the hydrogen yield first increases and then decreases with the increase of ball milling time. As the ball milling time is 1.0 h, the hydrogen yield reaches maximum value and is 92% for sample (a) and 96% for sample (b), respectively. It indicates that more Al is activated gradually with increasing ball milling time. So the hydrogen yield increases gradually. Fig. 3 is the XRD patterns of Al–40%CaO–5% NaCl ball-milled for different times. The results also show that the relative intensity of the diffraction peaks for Al phase has slight decrease as the ball milling time increases from 0.5 h to 1.0 h. By the calculation, the Al (111) crystallite size decreases from 69 nm to 57 nm. As well known, the smaller the crystallite size is, the higher the activity of Al is. Further prolonging the ball milling time to 2.0 h, the Al (111) crystallite size is decreased to 38 nm. But the hydrogen yield is greatly reduced to only 63% for sample (a) and 65% for sample (b), respectively. The phenomenon can also be found in reference [5,22,26–28]. The possible reason is that longer ball milling time can decrease the crystallite size of Al and increase the activity of Al. But the high activity aluminum is easily subjected to oxidation in air, which will reduce the hydrogen yield of Al-based materials. In addition, from the SEM image of Al–40%CaO–5% NaCl ball-milled for different time (Fig. 4), it is found that the particle size is decreased gradually when the ball milling time increase from 0.5 h to 1.0 h. But as the ball milling time reaches 2.0 h, larger agglomerates (with a diameter of particles >30 μm) can be observed (Fig. 4c). The larger particle size will reduce the surface accessible to water. This is one reason that the hydrogen yield is decreased after ball milling for 2.0 h. Based on above results, it is concluded that 1.0 h can be regarded as the optimal ball milling time.

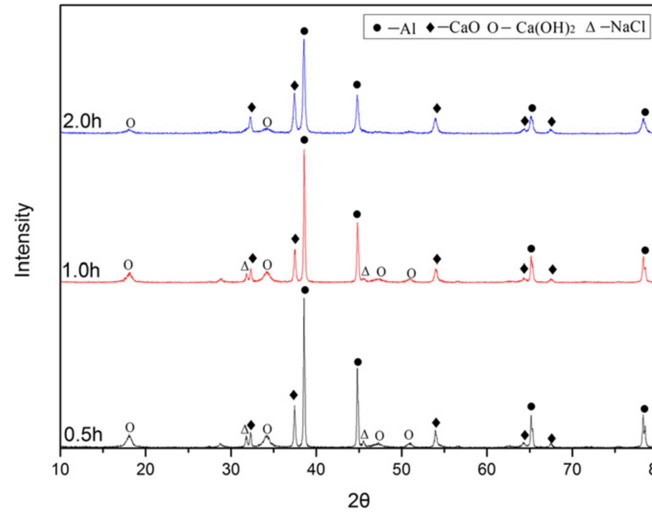

Fig. 3. XRD patterns of Al–40%CaO–5%NaCl ball-milled for different time.

3.2. *Effect of composition on the hydrogen generation*

The mixture of Al and CaO are ball-milled for 1.0 h, the prepared Al-based materials can also react with water to produce hydrogen. Fig. 5 is the hydrogen generation curves of Al-based materials with different CaO contents. As can be seen, with increasing CaO contents, the hydrogen generation rate is promoted and the hydrogen yield also increases steadily. As the CaO content is 15%, the total hydrogen yield is only 26% reacting for 5000 s. But when the CaO content increases to 30%, hydrogen yield can reach 76%, and the induction reaction period is reduced to about 1500 s. Further increasing the CaO content, the induction period is reduced to 1000 s and the hydrogen yield reach 86.7%. In the process,

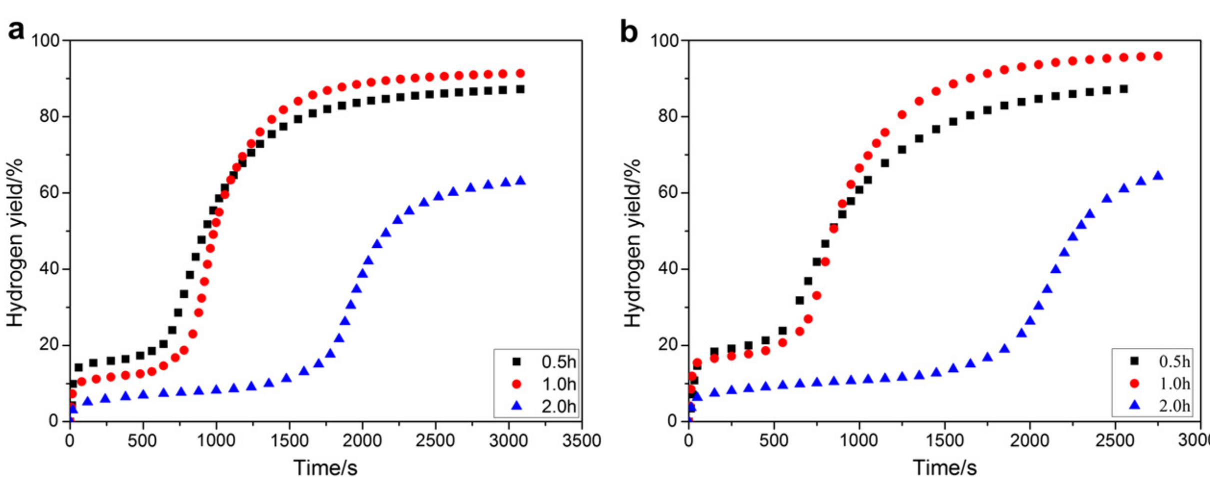

Fig. 2. Hydrogen generation curves for Al-based materials ball-milled for different time (a) Al–30%CaO–5%NaCl; (b) Al–40%CaO–5%NaCl.

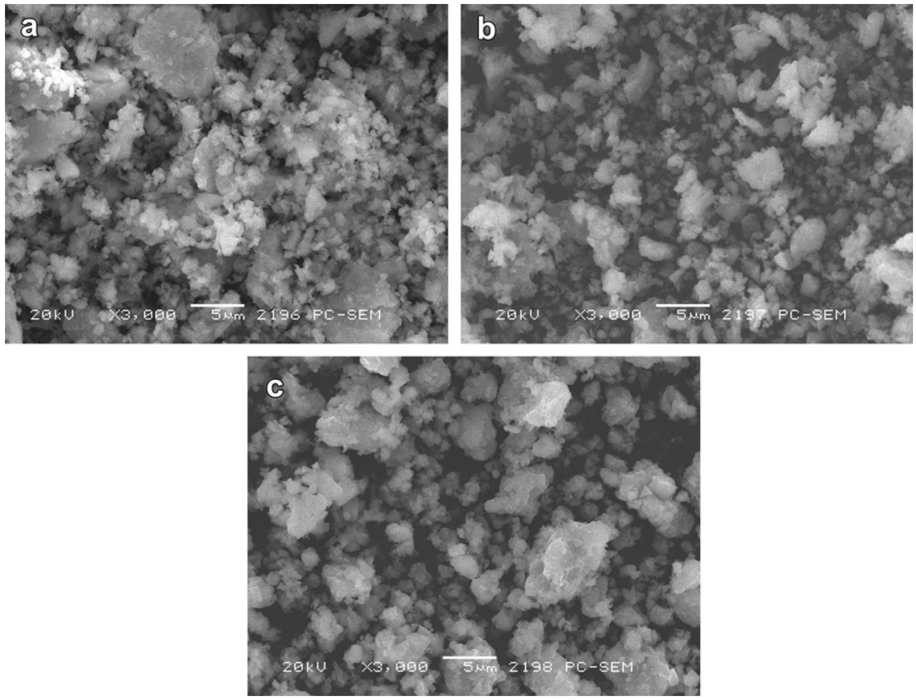

Fig. 4. SEM image of Al–40%CaO–5%NaCl ball-milled for different time (a) 0.5 h, (b) 1.0 h, (c) 2.0 h.

hydrogen generation is attributed to the reaction of Al with water. More Al participates in reaction, higher hydrogen yield can be achieved. Through analyzing the hydrogen yield of Al-based materials with different CaO contents, the hydrogen generation reaction can be described as follows:

$$2Al + 6H_2O = 2Al(OH)_3 + 3H_2 \quad (2)$$

$$CaO + H_2O = Ca(OH)_2 \quad (3)$$

$$Ca(OH)_2 = Ca^{2+} + 2OH^- \quad (4)$$

$$2Al + 2OH^- + 2H_2O = 2AlO_2^- + 3H_2 \quad (5)$$

After the mechanical ball milling, part metal Al is activated, and it can directly react with water to produce hydrogen according to equation (2). Additional Al is still not activated and cannot directly react with water. But CaO can react with water to produce OH^- according to equations (3) and (4). So the additional Al can react with OH^- to generate hydrogen through the reaction (5).

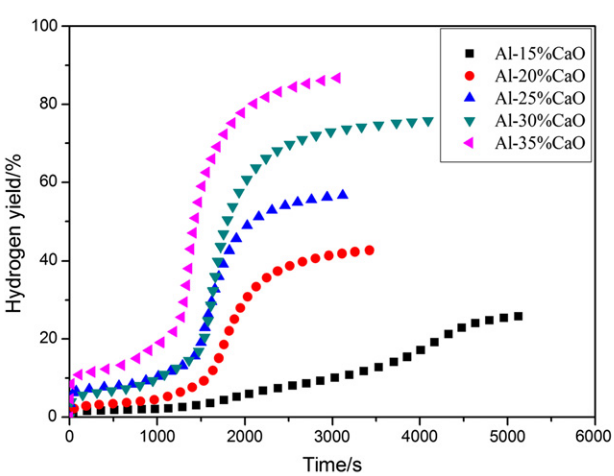

Fig. 5. Hydrogen generation curves for Al-based materials with different CaO contents.

It is clear that hydrogen is produced through the reactions (2) and (5). Therefore the total hydrogen yield is dependent on the activation degree of Al and the CaO content. So there are two measures, increasing CaO contents and improving activation degree of Al, for promoting the hydrogen generation. More CaO can provide more OH^- in the solution, so it can improve the hydrogen generation by the reaction (4). It has been verified by above research results.

In order to obtain more activated Al, NaCl is introduced into the Al–CaO powder mixture during the process of ball-milling. Fig. 6 is the hydrogen generation curves for Al-based materials with different NaCl addition. The hydrogen generation indeed is obviously promoted by adding NaCl. As the NaCl addition increases from 0% to 10%, the induction period for Al–25%CaO system decreases from 1500 s to 600 s. The reaction rate is increased greatly and the total hydrogen yield can reach 100%. In the Al–35% CaO system, as the NaCl addition reaches 7%, the induction period is also obviously reduced and the total hydrogen yield reaches 100%. The results show that the NaCl addition indeed can increase the activity of Al and is beneficial to increase the hydrogen generation rate and yield. The roles of NaCl mainly include as follows: (1) In the preparation process of Al-based materials, the NaCl particles is well dispersed on the surface and crack of Al particle by ball-milling. The dispersed NaCl particles can effectively inhibit the cold welding phenomenon of metal and prevent the aggregation of Al particles. Therefore, the specific surface area of Al particles will be increased by ball-milling. Large specific surface area of Al particles has high reactivity and can accelerate the reaction with water to produce hydrogen. The more the NaCl adds, the larger the specific surface area of Al particles is, and the higher the reactivity of Al-based materials is. (2) The NaCl addition can increase the conductivity of reaction solution for hydrogen production of Al-based materials.

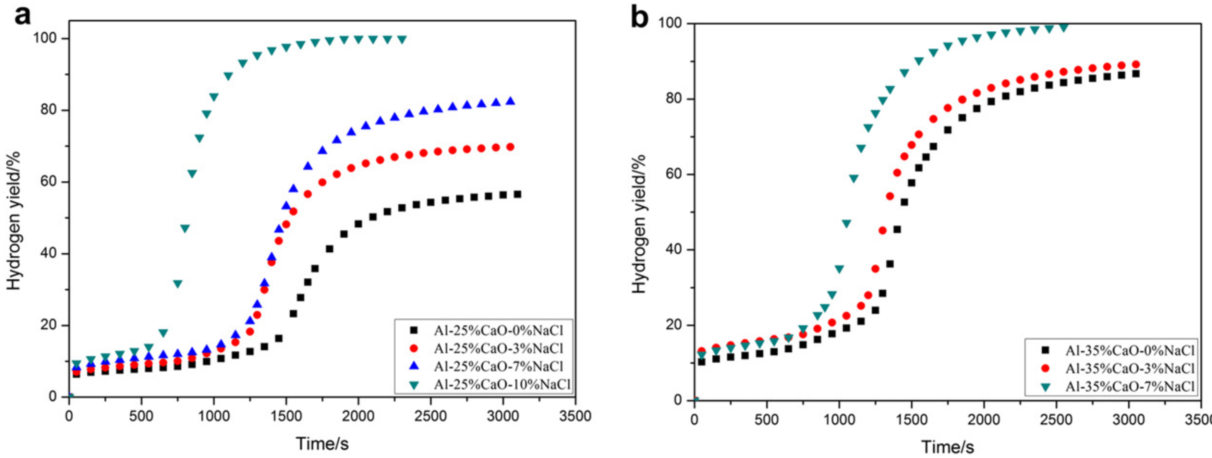

Fig. 6. Hydrogen generation curves for Al-based material with different NaCl addition.

In addition, Cl^{-} easily penetrates into aluminum oxide film to reach the surface of Al particle and cause the corrosive pitting of Al, which make the electrode potential of Al become more negative. The Al-corrosion will become more easy [23]. Therefore, the NaCl addition can improve the reactivity of Al-based materials and accelerate the Al-corrosion and hydrogen generation.

Al–CaO–7%NaCl powder mixture ball-milled for 1.0 h is used to produce hydrogen, and the effect of CaO content on the hydrogen generation is presented in Fig. 7. With increasing CaO content, the induction period is gradually reduced, and the hydrogen generation rate is promoted. As the CaO content reaches 45%, 100% of hydrogen yield can be achieved within 2500 s. The research results further indicate that increasing CaO content is beneficial to hydrogen generation. The effect of NaCl addition and CaO content on the hydrogen yield is showed in Fig. 8. It is very obvious that increasing CaO content or NaCl addition is helpful to improve the hydrogen yield of Al-based materials. As can be seen in Fig. 8, when the CaO content is less than 30%, the hydrogen yield is clearly affected by the NaCl addition. In order to achieve a higher hydrogen yield, it is essential to adding 10% or even more NaCl. For example, as the CaO content is 25%, 10% NaCl addition can achieve 100% hydrogen yield. But as the CaO decreases to 15%, 10% NaCl addition can only gain 86% hydrogen yield. It is very likely for the material with 15% CaO to reach 100% hydrogen yield by further increasing the NaCl addition. Furthermore, it is also found that when the CaO content is more than 30%, the effect of NaCl addition on the hydrogen yield is not so obvious. Before adding NaCl, the hydrogen yield is much high and almost reach about 90%. It is likely that adding a small amount of NaCl can increase the hydrogen yield to 100%. The results show that 7% NaCl addition for Al–40%CaO and 5% NaCl addition for Al–45% CaO are enough to gain 100% hydrogen yield. It indicates that as the CaO content of Al-based materials increases, the NaCl addition may decrease accordingly.

Although increasing CaO content or NaCl addition is helpful to improve the hydrogen generation rate and yield but cannot produce hydrogen by itself, too much CaO content or NaCl addition will reduce the hydrogen yield of unit mass Al-based materials. Table 1 is the hydrogen yield of unit mass Al-based materials with different composition. Based on above research, in order to obtain a higher hydrogen yield of unit mass Al-based materials, 20%–25% CaO content and 10% NaCl addition are regarded as more appropriate composition.

3.3. *Effect of different water solution on the hydrogen generation*

Different water solution may have different effects on the hydrogen generation of Al-based materials. In order to investigate

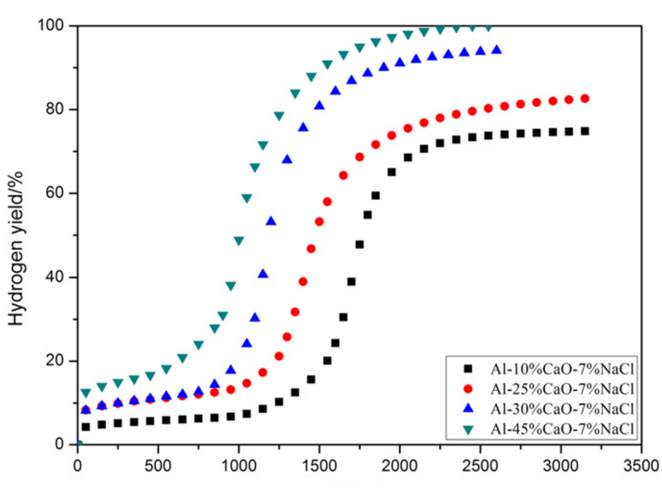

Fig. 7. Hydrogen generation curves for Al-based material with different CaO contents.

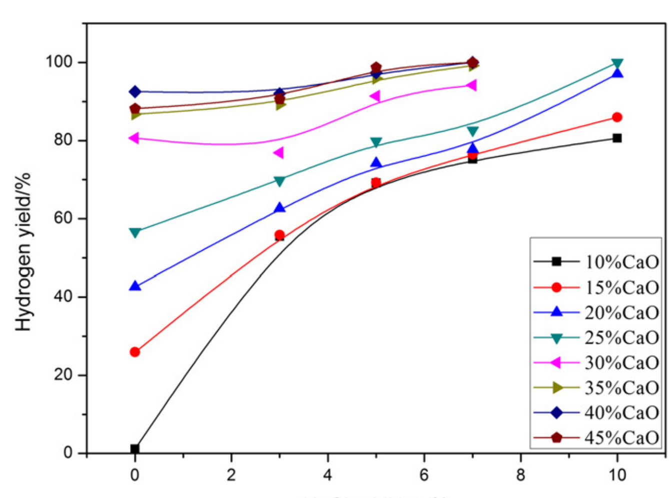

Fig. 8. Effect of different CaO contents and NaCl addition on hydrogen yield.

Table 1
Hydrogen yield of unit mass Al-based materials with different composition.

ml H_2/g of Al-based materials		CaO							
		10%	15%	20%	25%	30%	35%	40%	45%
NaCl	0%	14.2	299.6	463.4	577.3	766.8	765.8	754.0	658.8
	3%	655.2	622.1	654.8	682.8	699.9	751.4	712.3	639.7
	5%	798.4	752.6	755.8	759.2	807.0	781.8	727.1	670.7
	7%	868.7	831.1	792.8	786.1	831.7	808.4	747.1	679.2
	10%	930.7	934.3	989.0	950.8	–	–	–	–

the effect, the Al-based materials react with different salt solutions to produce hydrogen. Fig. 9 is the hydrogen generation curves for Al–40%CaO–7%NaCl reacting with different salt solutions. The results show that the hydrogen generation is obviously promoted in the NaCl, Na_2SO_4 and $CaCl_2$ solution. The induction period almost disappears in the 1.0 mol L^{-1} NaCl and 1.0 mol L^{-1} Na_2SO_4 solution. The induction period is 1100 s in the pure water. In the 0.5 mol L^{-1} $CaCl_2$ solution, the induction period is only about 250 s. It is possible to reduce the induction period by further increasing the concentration of $CaCl_2$ solution. In addition, the hydrogen yield can also reach 100% in these solutions. In the NaCl and $CaCl_2$ solution, the hydrogen generation is promoted mainly due to the existing of chloride ion in the reaction process [23,24]. It's obviously that the SO_4^{2-} breaks the solubility equilibrium of $Ca(OH)_2$ and a great amount of OH^- can be produced according to the reaction (6), so the reaction (5) can be promoted.

$$Ca(OH)_2 + SO_4^{2-} = CaSO_4 + 2OH^- \quad (6)$$

However, in the 0.5 mol L^{-1} $MgCl_2$ solution, the hydrogen generation is affected greatly, and its hydrogen yield is reduced to only 25.5%. For the similar reason, Mg^{2+} can also change the solubility equilibrium of $Ca(OH)_2$. But it decrease the OH^- concentration of solution due to the formation of $Mg(OH)_2$, which will decrease the hydrogen yield. In addition, the formed $Mg(OH)_2$, covered on the surface of Al-based material, also prevents the hydrogen generation. So in order not to affect the hydrogen generation, the Al-based materials should avoid reacting with the water containing Mg^{2+}. The above effects of different salt solution on the hydrogen generation have been verified in reference [24].

3.4. Effect of initial water temperature on the hydrogen generation

Temperature is a key factor for the chemical reaction. Generally the chemical reaction rate is accelerated by increasing the temperature. In order to investigate the hydrogen generation of Al-based materials under different conditions, Al-based materials react with pure water at different initial temperatures. Al–25%CaO–10%NaCl reacts with pure water to produce hydrogen at different temperatures, and the hydrogen generation curves are showed in Fig. 10. The results show that the induction period increases from 10 °C to 30 °C, and then decreases with the increase of initial water temperature from 30 °C to 80 °C. In the water at 30 °C, the induction period is the longest and reaches about 600 s. As the initial water temperature increases to 80 °C, the induction period is almost reduced to 0 s. Generally, the induction period depends on the rate of reactions (2) and (5). The faster the reaction, the shorter the induction period becomes. To the reaction (2), higher temperature is helpful to increase its reaction rate. So the induction period can be decreased by increasing the water temperature. As well known, the solubility of $Ca(OH)_2$ is decreases with the increase of water temperature. In the lower temperature, $Ca(OH)_2$ can release more OH^- is in the solution. So the lower water temperature is beneficial to improve the rate of reaction (5). The induction period can also be reduced by decreasing the initial water temperature. Therefore, the induction period can be controlled by adjusting the initial water temperature.

Actually, the hydrogen generation reactions of Al-based materials belong to exothermic reaction. A great amount of heat can be produced during the process of hydrogen generation, and the water temperature will increase gradually. After the induction period, the hydrogen generation rate is mainly attributed to the reaction (2). In addition, the hydrogen yield varies with the initial water

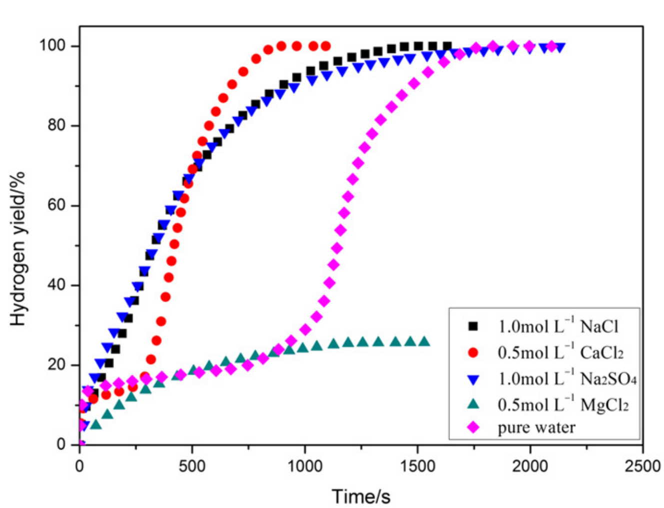

Fig. 9. Hydrogen generation curves for Al–40%CaO–7%NaCl reacting with different salt solutions.

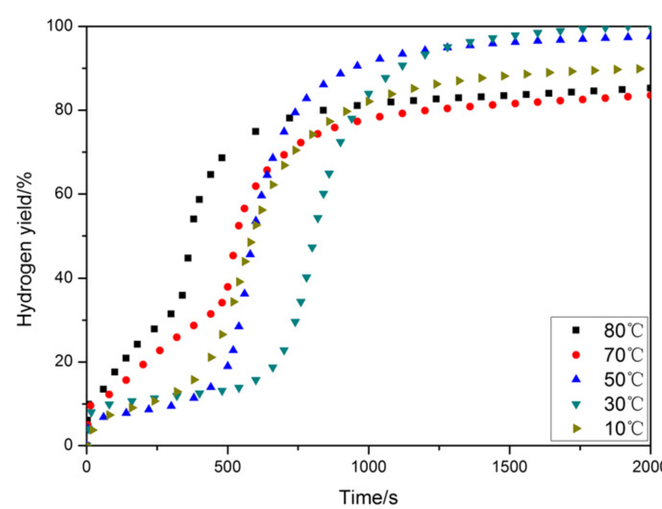

Fig. 10. Hydrogen generation curves for Al–25%CaO–10%NaCl reacting with pure water at different initial temperature.

temperature. In the water at 30 °C, the hydrogen yield of Al-based materials can reach 100% within 2000 s. But in the water at 10 °C and 80 °C, the hydrogen yield decreases to 90% and 85%, respectively. Through several experiments, the results show good reproducibility. Further analyzing the experimental data, it is found that the hydrogen yield is related to the induction period. The longer the induction period, the higher the hydrogen yield.

Hydrogen yield is ascribed to the consumption of activated and unactivated Al. Generally, the activated Al can be completely consumed according to the reaction (2) at higher temperature. So, the hydrogen yield depends on the consumption of unactivated Al. A longer induction period can ensure that more unactivated Al can react to produce hydrogen according to the reaction (5). Based on above research results, it is possible that a higher hydrogen yield can be obtained by controlling the initial water temperature.

3.5. Effect of air exposure on the hydrogen generation

Through above researches, it is found that the Al-based materials has very good activity and can split water to produce hydrogen. How to safely store the Al-based material has become a very important problem. H_2O and O_2 are the two main factors, which probably affect the hydrogen generation of Al-based material. In order to investigate the effect of H_2O and O_2 on the hydrogen generation, Al-based materials are placed in air with relative humidity of 50% at 30 °C for different time and then react with water to produce hydrogen. The hydrogen generation curves of Al–25%CaO–10%NaCl air exposed for different time are showed in Fig. 11. As the air exposure time is 5.0 h, the hydrogen yield decreases from 100% to 92.7%. Further prolonging the air exposure time, the hydrogen yield almost has no obvious changes. As the Al-based materials respectively expose for 10 h, 20 h and 40 h in air, its hydrogen yield yet can be kept at 91.5%, 93.5 and 89%, respectively. The decrease of hydrogen yield is mainly due to the oxidation of Al during the process of air exposure. The activated Al is easily oxidized into Al_2O_3 by air and loses the capacity for producing hydrogen. The CaO and the formed Al_2O_3 layer cover on the surface of Al-based material particles and can prevent the further oxidation of Al. So the hydrogen yield doesn't continue to decrease with increasing air exposure time. Fig. 12 is the XRD patterns of Al–25% CaO–10%NaCl air exposed for different time. The results show that the relative intensity of the diffraction peaks for Al phase decreases with the increase of air exposure time from 0 h (Fig. 12a) to 5 h (Fig. 12b). It is confirmed that Al is indeed oxidized. But further

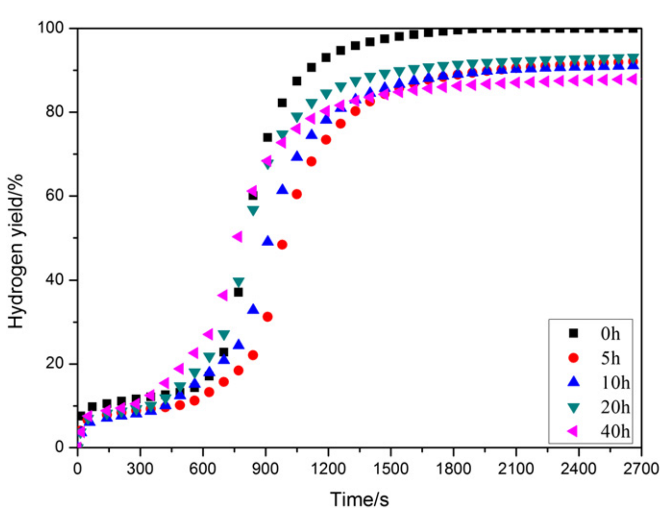

Fig. 11. Hydrogen generation curves for Al–25%CaO–10%NaCl air exposed for different time.

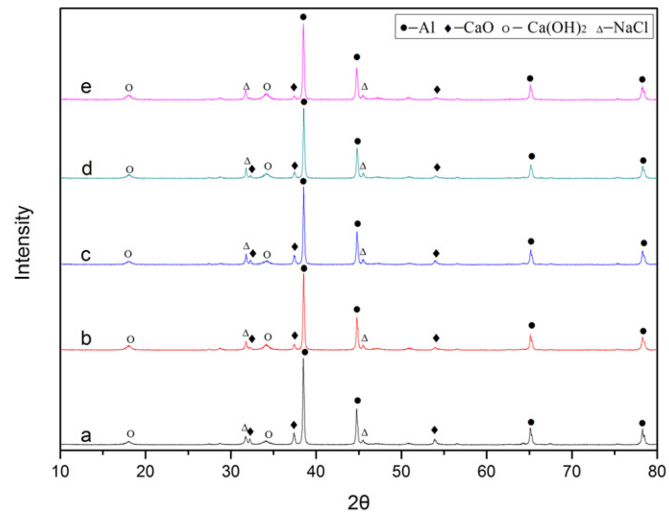

Fig. 12. XRD patterns of Al–25%CaO–10%NaCl air exposed for (a) 0 h, (b) 5 h, (c) 10 h, (d) 20 h and (e) 40 h.

prolonging air exposure time, the diffraction peaks of Al phase nearly has no changes. The XRD results are consistent with above results of hydrogen generation.

Above research results show that Al-based materials have a good air oxidation resistance. Actually, CaO in the Al-based materials mainly play two important roles. First, after ball-milling, CaO covers on the surface of Al particles, which can prevent the air oxidation. Second, the hydrolysis of CaO can provide the OH^- for the reactions (5) and (7). Although a layer of Al_2O_3 forms on the surface of Al particles in air, it can be dissolved according to the reaction (7). So the hydrogen generation can continue to proceed.

$$Al_2O_3 + 2OH^- = 2AlO_2^- + H_2O \tag{7}$$

4. Conclusion

A kind of new hydrogen production material, Al-based materials, is successfully prepared by ball milling the Al, CaO and salt powder mixtures. The research results show that longer ball milling time is beneficial to decrease the crystallite sizes of Al and to increase the activity of Al. But the overlong ball milling time easily cause the oxidation of Al and consequently decreases the hydrogen yield. 1.0 h is regarded as the optimal ball milling time. The CaO content and NaCl addition are two key factors for improving the hydrogen generation. Increasing the CaO content and NaCl addition is beneficial to improve the hydrogen generation and yield. The NaCl addition depends on the CaO content in the Al-based materials. With increasing CaO content, the NaCl addition can be reduced accordingly, and a high hydrogen yield can also be gained. The Al-based material can react with different water solutions at different temperature. Chloride ions and sulfate ions can obviously promote the hydrogen generation rate. But Mg^{2+} ions will decrease the hydrogen yield due to its strong affinity to OH^-. Even in water at 10 °C, the Al-based material can split water to produce hydrogen. The maximum hydrogen yield is gained at 30 °C. The Al-based materials have a good air oxidation resistance due to the existence of CaO. So storing the Al-based materials in air with relative humidity of 50% at 30 °C for 40 h, the hydrogen yield is still kept at 89%.

Acknowledgments

This work is financially supported by Postdoctoral Science Foundation of Central South University and the Fundamental Research Funds for the Central Universities (2012QNZT020).

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